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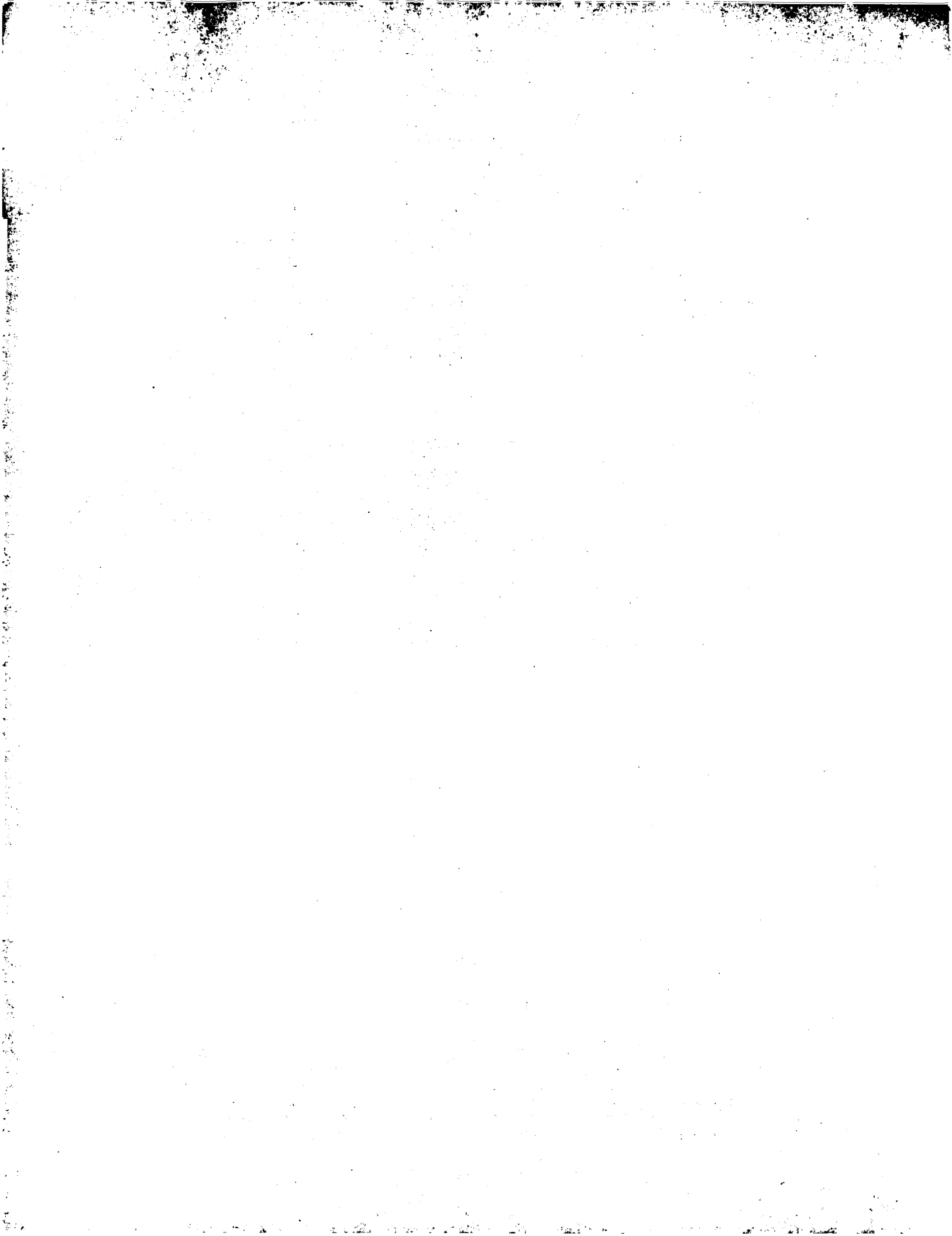
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(54) Title: CROSS-REFERENCE TO RELATED APPLICATIONS

(57) Abstract: A fuel cell having an electrode and/or catalyst formed from a nano-carbon material, such as fullerene, carbon nanotube, carbon nanohorn, carbon nano-fiber or metal encapsulated fullerene. Such fuel cells may not use platinum in the electrode or catalyst, or may use platinum in small amounts. The efficiency of the fuel cell may be increased by applying external energy to the electrode and/or catalyst. A cationic membrane may be positioned between the cathode and anode of the fuel cell. Also disclosed is an improved method for generating electricity from a fuel cell having at least one electrode formed from a nano-carbon material. To increase the efficiency of the fuel cell, the electrode or catalyst containing nano-carbon material may be irradiated with the blue color diode light, or an electric current may be directed to the nano-carbon material.



FUEL CELL

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims priority under 35 U.S.C. § 119 to Japanese Application Ser. No. 2000-346526, filed November 14, 2000, and to Japanese Application Ser. No. 2000-384120, filed December 18, 2000, both applications are
5 hereby incorporated herein by reference.

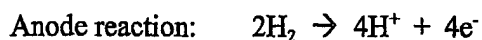
BACKGROUND OF THE INVENTION

This invention relates to electrochemical fuel cells and methods for making an electrochemical fuel cell. More particularly, the present invention is directed to a fuel cell system having electrodes incorporating hydrogen storable
10 substances, such as fullerenes, carbon nanotubes, carbon nanohorns, carbon nanofibers and metal encapsulated fullerenes.

Fuel cells combine hydrogen and oxygen without combustion to form water and to produce direct current electric power. The process can be described as electrolysis in reverse. Fuel cells have potential for stationary and portable power
15 applications; however, the commercial viability of fuel cells for power generation in stationary and portable applications depends upon solving a number of manufacturing, cost, and durability problems.

Electrochemical fuel cells convert fuel and an oxidant to electricity and a reaction product. A typical fuel cell consists of a membrane and two
20 electrodes, called a cathode and an anode. The membrane is sandwiched between the cathode and anode. Fuel, in the form of hydrogen, is supplied to the anode, where a catalyst, such as platinum and its alloys, catalyzes the following reaction:

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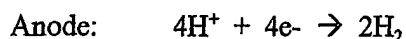
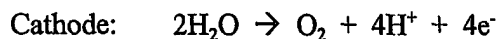


At the anode, hydrogen separates into hydrogen ions (protons) and electrons. The protons migrate from the anode through the membrane to the cathode. The electrons migrate from the anode through an external circuit in the form of electricity. An oxidant, in the form of oxygen or oxygen containing air, is supplied to the cathode, where it reacts with the hydrogen ions that have crossed the membrane and with the electrons from the external circuit to form liquid water as the reaction product. The reaction is typically catalyzed by the platinum metal family. The reaction at the cathode occurs as follows:



Thus, the fuel cell generates electricity and water through the electrochemical reaction.

In a known hydrolysis cell, a cationic membrane is positioned between platinum containing electrodes. In such a hydrolysis cell, the following electrochemical reactions occur:



The most promising fuel cells for widespread transportation use are Proton Exchange Membrane (PEM) fuel cells. PEM fuel cells operate at relatively low temperatures, have a relatively fast response time and have relatively high energy density compared to other fuel cell technologies. Current PEM fuel cells rely on flat-plate electrodes. Any fuel cell design should: (a) allow for supply of the reactants (typically, hydrogen and oxygen); (b) allow for mass transport of the

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reaction product (water) and associated inert gases (nitrogen and carbon dioxide from air); and (c) provide electrodes to support the catalyst, to collect electrical charge, and to dissipate heat. Electrical and thermal resistance, reactant pressures, temperatures, surface area, catalyst availability are some of the major factors affecting the performance and efficiency of a fuel cell. Some problems encountered in the use of PEM fuel cells include the need to reduce thermal stress concentrations, and the need to increase integrity and performance of the fuel cell.

In recent years, new "nano" carbon materials have been produced, and they may be considered as the future storage material of hydrogen for a new generation energy producing and storage devices. However, it is difficult to put compressed hydrogen in a container constructed from such "nano" carbon materials. For example, certain hydrogen storable substances, such as a carbon nanotube or a carbon nanofiber, have a storage capacity of about ten kilograms/meter³ (kg/m³). Since the chargeable ratio is about fifty percent, then the actual stored hydrogen is five kg/m³. Especially for the use of hydrogen fuel cells in automobiles, airplanes and other moving transports, it is necessary to safely store hydrogen, so as to avoid hydrogen combustion in the fuel cell. In addition, a system is needed to quickly supply hydrogen to the fuel cell anode.

When hydrogen storable metal compounds are used, repeated input and output of hydrogen leads to degradation of the compound. Further, the mass ratio of the storable hydrogen to the metal used is very low. Consequently, when the hydrogen storable metal compounds contain precious metals, such as platinum, the cost is prohibitively high, and thus, not suitable of such fuel cells for most applications of the technology.

What has been needed and heretofore unavailable is a safe, efficient and cost effective fuel cell, which is suitable for mass production. The present invention satisfies this need.

SUMMARY OF THE INVENTION

Briefly, and in general terms, the present invention is directed to a fuel cell having an electrode or catalyst formed from a nano-carbon material, such as fullerene, carbon nanotube, carbon nanohorn, carbon nanofiber and metal
5 encapsulated fullerene. Such an encapsulated fullerene may include a metal from the platinum metal family, including platinum, palladium, rhodium, iridium, osmium and ruthenium. The present invention is applicable to a sandwich-type electrolyte fuel cell, having a first electrode, a second electrode formed from a nano-carbon material and an ion exchange membrane positioned between the first
10 electrode and the second electrode. The efficiency of the fuel cell may be increased by applying external energy to the electrode and/or catalyst.

The present invention relates to fuel cells utilizing hydrogen as the fuel and oxygen containing air as the oxidant. An improvement over previously known fuel cells is that at least one electrode or the catalyst is formed from a
15 hydrogen storable carbon material, such as fullerenes, carbon nanotubes, carbon nanohorns, nanofibers, metal encapsulated fullerenes. Such a fuel cell may include a cationic membrane positioned between the cathode and anode. To reduce the cost of the catalyst, fuel cells constructed according to the present invention may not use platinum at all, or may use platinum in very small amounts.

20 The present invention further includes an improved method for generating electricity from a fuel cell having a first electrode and a second electrode, such that at least one electrode is formed from a nano-carbon material. An ion exchange membrane may be positioned between the first electrode and the second electrode. Oxygen is directed to the one electrode, and hydrogen is directed
25 to the other electrode. To increase the efficiency of the fuel cell, the electrode containing nano-carbon material is irradiated with blue color diode light, or electric current is directed to the nano-carbon electrode.

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Other features and advantages of the invention will become apparent from the following detailed description.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

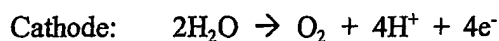
The present invention is directed to constructing the electrodes and/or the catalyst material of an electrochemical fuel cell unit using hydrogen storable (absorbable) carbon material, such as, but not limited to, fullerenes, carbon nanotubes, carbon nanofibers, and/or metal encapsulated fullerenes incorporating platinum family metals, collectively, "nano-carbon materials". Embodiments of the present invention include increasing the efficiency of the catalytic function of the fuel cell by irradiating the catalyst with blue color diode light, and/or by conducting electric current to the catalyst. The catalyst may be incorporated into an electrode, or may be a separate member of the fuel cell. The present invention further includes methods of producing the fuel cells using inexpensive methodology, when the electrochemical fuel cells are produced in mass quantities. The present invention is primarily used for fuel cell electric power generation, and incorporates into the fuel cell one or more nano-carbon materials having hydrogen absorbable properties, for example, from the fullerene family.

Specifically, the present invention relates to PEM fuel cells utilizing hydrogen as the fuel and oxygen containing air as the oxidant. An improvement over previously known fuel cells is that the present invention incorporates into one or both electrodes, which may include the catalyst, or into the catalyst some hydrogen absorbable carbon material, such as fullerenes, carbon nanotubes, carbon nanohorns, nanofibers, metal encapsulated fullerenes (alone or in combination). Embodiments of a fuel cell incorporating the present invention include a membrane between the cathode and anode constructed from a cationic material.

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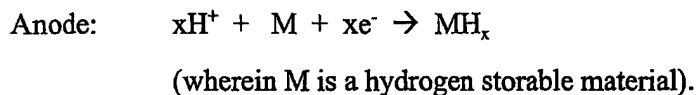
A fuel cell needs a constant supply of fuel (hydrogen) to the anode. Thus, the fuel circulation system can become very complicated. To solve some of the fuel circulation problem, one aspect of the present invention includes incorporating a hydrogen storable substance at the anode side of the fuel cell. A

5 hydrolysis cell produces hydrogen and oxygen; however, in some applications, only oxygen is used and the hydrogen is not needed. If the cathode is operated using the following formula:



and the anode is constructed to include a hydrogen storable (absorbable) substance,

10 the following process occurs, and there will not be free hydrogen:



Known hydrogen storable substances include LaNi_5 , $\text{MmNi}_x\text{Al}_y\text{Mn}_z$ (wherein Mm is the so called "Misshu Metal") and NiTi alloys. When such

15 hydrogen storable metals are used in a fuel cell having a cationic membrane that is a very strong acid, oxidation occurs to the metal substance, and it is not practical to use such fuel cells in a commercial environment. Moreover, platinum is used in most such fuel cells. However, the production of such fuel cells is very limited, since platinum is a very expensive and rare precious metal. Fuel cells constructed

20 according to the present invention may not use platinum at all, or may use platinum in very small amounts. This reduction or elimination in the use of platinum is accomplished by using a fullerene, carbon nanotube, carbon nanohorn, carbon nanofiber or metal encapsulated fullerene to generate active hydrogen and produce an efficient fuel cell system.

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To overcome some of the aforementioned deficiencies of current fuel cell technology, the present invention is directed to fuel cells using electrodes incorporating one or more substances that are hydrogen storable elements, such as fullerenes, carbon nanotubes, carbon nanohorns, carbon nanofibers and metal encapsulated fullerenes. The metal encapsulated fullerenes include platinum group metals, which possess the capability of the catalytic function of separating a hydrogen molecule to a proton and an electron. The efficiency of the catalytic function may be increased by applying external energy, such as radiating the catalyst with blue light and/or conducting an electric current to the catalyst. One embodiment of a fuel cell stack of the present invention includes a membrane positioned between two electrodes (a cathode and an anode), such that one electrode contains a metal encapsulated fullerene that is capable of the catalytic function and the other electrode does not contain the metal encapsulated fullerene.

In recent years, special attention has been paid to new carbon substances like fullerene. Different fullerene's chemical representation are often shown as C_{60} , C_{70} , C_{120} , etc. These carbon compounds are each formed with a hexagon or five-corners shape. One of the most well known substances is C_{60} , a twelve times five-corners shape, and thirty-two times hexagon shape formation, commonly called a "buckminster fullerene" or "buckyball." The characteristics of fullerenes are known to produce doping alkaloid metal in between frames of M_3C_{60} (wherein M is an alkaloid metal, such as potassium, rubidium, etc.), and to encapsulate such metals as lanthanum and calcium in the formation of compounds like LaC_{82} , La_2C_{82} and C_{60} .

A fullerene molecule cannot be used alone as catalyst for a hydrogen molecule to separate hydrogen into a proton and a electron. Similarly, a fullerene molecule cannot be used alone to store hydrogen released during a hydrolysis reaction. However, by adding a functional catalyst, such as platinum group metals or another carbon family substance, the compound can be used to produce very

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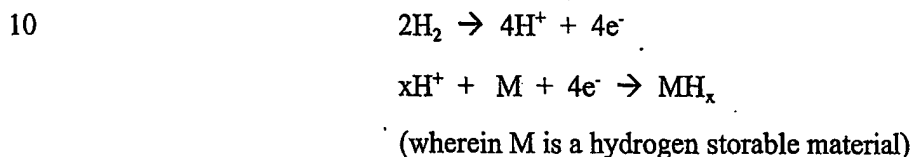
functional electrodes, or the compound can be used to store hydrogen. Such a fullerene-platinum compound is very durable for use in the extreme acid conditions associated with a cationic membrane.

Fuel cells constructed according to the present invention can be
5 utilized for vast area of electrical generation purposes. The electrodes containing fullerene molecules may be mixed with platinum group metals compounds or common fuel cell carbon substances, such as graphite. Active carbon containing platinum group metals may mix with fullerene molecules by using polytetrafluoroethylene (PTFE) like a glue to adhere the electrodes on either side of
10 a cationic membrane (electrolyte). Also, fullerene electrodes may be adhered to a cationic membrane by using a bio-solvent and water mixture as a glue. For constructing the cationic membrane, a perfluorocarbon or stilenge-benil-benzine equal volume mixture is used as the base for the membrane. Ion exchange in the membrane is accomplished by using a sulfonic acid (HSO_3) foundation or kalopon-
15 acid foundation .

An oxygen-fullerene based fuel cell may be configured by constructing the anode from a compound including one or more fullerene molecules and one or more hydrogen storable (absorbable) substances, such that oxygen or air is supplied to the cathode. Hydrogen may be stored in the anode before or after
20 making fullerene-containing electrode. Similarly, a fullerene-containing anode may be used for constructing a hydrogen battery in a closed container. Such a battery can be disposed of after discharge, or can be recharged with hydrogen from an external source through an intake hole for reuse of the battery. The use of such a fullerene-containing anode that stores hydrogen in a fuel cell or battery eliminates
25 the need for complicated gas feeding and extracting circulation systems. Thus, such fuel cells and batteries may be economical and convenient for some particular applications.

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Also, the oxygen electrode (cathode) may be used to supply hydrogen to the fullerene-containing electrode (anode). For example, if a platinum encapsulated carbon family substance is used for the oxygen electrode (combining oxygen with hydrogen to form water), then that substance also may be useable as a hydrogen electrode (forming hydrogen ions). In such an application, instead of feeding oxygen or air to the cathode, hydrogen is fed to the cathode from outside, and electricity is conducted between the cathode and the anode so as to store hydrogen in the anode by following electrochemical reaction:



In an embodiment of a fuel cell or battery configured with electrodes that contain platinum encapsulated fullerene molecules, the catalytic function of the electrodes may be increased by radiating light energy, for example blue diode light, onto the fullerene molecules.

In another embodiment of a fuel cell system, the stack is constructed from a cathode made from a porous conductive material, an anode also made from a porous conductive material and cationic membrane positioned between those electrodes. Such a membrane may be fifty millimeters (mm) in diameter, having a 0.2 mm thickness, and may be constructed from a "perfluorosulfonic acid PTFE copolymer" or other solid polymer electrolyte, for example, the product having a trade name: NAPHION 117, made by E.I. Du Pont de Nemours and Company. The metallic catalyst may be prepared using two percent platinum active-carbon in a dispersion of polytetrafluoroethylene and NAPHION-117. An alcohol and water mixture may be used for binding the catalyst materials onto the NAPHION material. The anode may be constructed from ten percent platinum encapsulated

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fullerene C₆₀ in a dispersion of polytetrafluoroethylene and NAPHION-117. An alcohol and water mixture may be used for binding the anode onto the NAPHION material. Both the cathode and the anode may be thirty mm in diameter. Since there is almost no hydrogen in the fullerene electrode when it is initially
5 constructed, hydrogen must be charged to the anode before operational use of the fuel cell.

A catalyst for the electrodes is necessary to construct an efficient fuel cell using fullerene family carbon molecules. This is especially true when using fuel cells for automobile use, even when pure hydrogen is used at the anode, and the
10 oxygen side of the electrode (cathode) must be very efficient. For a hydrogen and oxygen fuel cell electrode system, the electrode (anode) on the hydrogen (fuel) side may be constructed without using platinum, if the carbon monoxide output of the fuel cell is about one thousand parts-per-million. At the oxygen (air) electrode (cathode) a passing voltage decline of about one-hundred millivolts decrease is
15 desirable. The efficiency of the fuel cell possibly may be increased by adjusting the fullerene content amount, and/or by changing and trying different carbon family substances.

As mentioned above, the present invention of an improved fuel cell stack includes constructing one of the electrodes with a fullerene material mixed
20 with a metal capable of catalytic function. A fullerene molecule itself is not able to store hydrogen, but by using platinum group metals in the compound, fullerene molecules can electrochemically store hydrogen. In addition, when fullerene carbon family substance are used to construct an electrode, such electrodes are very durable for use with acid containing solid ion-based conductor, and such electrodes
25 will not be easily damaged. Thus, a long life fuel cell may be built. If the present invention is utilized for a fuel cell, such that only oxygen or air is sent to the cathode side, then electricity can be produced. Hydrogen may be stored at the anode side before commencing operation of the fuel cell, and no need to supply

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hydrogen to the anode. Therefore, the system and structure of the fuel cell may become very simple.

It will be apparent from the foregoing that, while particular forms of the invention have been illustrated and described, various modifications can be
5 made without departing from the spirit and scope of the invention. Accordingly, it is not intended that the invention be limited, except as by the appended claims.

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WHAT IS CLAIMED IS:

1. A fuel cell, comprising:
an electrode formed from a carbon material selected from the group consisting of fullerene, carbon nanotube, carbon nanohorn, carbon nanofiber and metal encapsulated fullerene.
2. The fuel cell of claim 1, wherein the metal encapsulated fullerene includes a metal from the platinum metal family, wherein the electrode is capable of hydrogen catalyst.
3. The fuel cell of claim 2, wherein the platinum family metal is selected from the group consisting of platinum, palladium, rhodium, iridium, osmium and ruthenium.
4. The fuel cell of claim 1, further comprising means for irradiating the electrode with blue color diode light.
5. The fuel cell of claim 1, further comprising means for conducting electric current to the electrode.
6. A sandwich-type electrolyte fuel cell, comprising:
a first electrode;
a second electrode formed from a carbon material selected from the group consisting of carbon nanotube, carbon nanohorn and carbon nanofiber; and
an ion exchange membrane positioned between the first electrode and the second electrode.

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7. The fuel cell of claim 6, wherein the first electrode functions as a cathode and the second electrode functions as an anode.
8. The fuel cell of claim 6, wherein the first electrode functions as an anode and the second electrode functions as a cathode.
9. The fuel cell of claim 6, wherein the ion exchange membrane includes a perfluorocarbon ion exchange resin containing sulfonic acid groups.
10. The fuel cell of claim 9, wherein the ion exchange membrane is formed from NAPHION.
11. The fuel cell of claim 6, wherein the first electrode is formed from a carbon material selected from the group consisting of carbon nanotube, carbon nanohorn and carbon nanofiber.
12. The fuel cell of claim 6, wherein the first electrode is formed from a metal encapsulated fullerene having a metal from the platinum metal family.
13. The fuel cell of claim 6, further comprising means for irradiating the second electrode with blue color diode light.
14. The fuel cell of claim 6, further comprising means for conducting electric current to the second electrode.
15. The fuel cell of claim 11, further comprising means for irradiating the first electrode and the second electrode with blue color diode light.

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16. The fuel cell of claim 6, further comprising means for conducting electric current to the first electrode and to the second electrode.

17. A sandwich-type electrolyte fuel cell, comprising:
a first electrode;
a second electrode formed from a fullerene encapsulated with a platinum family metal; and

5 an ion exchange membrane positioned between the first electrode and the second electrode.

18. The fuel cell of claim 17, wherein the platinum family metal is selected from the group consisting of platinum, palladium, rhodium, iridium, osmium and ruthenium.

19. A fuel cell, comprising:
a catalyst formed from a carbon material selected from the group consisting of fullerene, carbon nanotube, carbon nanohorn, carbon nanofiber and metal encapsulated fullerene.

20. The fuel cell of claim 19, wherein the metal encapsulated fullerene includes a metal from the platinum metal family.

21. The fuel cell of claim 19, further comprising means for irradiating the catalyst with blue color diode light.

22. The fuel cell of claim 19, further comprising means for conducting electric current to the catalyst.

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23. A fuel cell, comprising an electrode formed from a nano-carbon material.

24. A fuel cell, comprising a catalyst formed from a nano-carbon material.

25. A method for generating electricity from a fuel cell, comprising:
providing a catalyst formed from a carbon material selected from the group consisting of fullerene, carbon nanotube, carbon nanohorn, carbon nanofiber and metal encapsulated fullerene.

26. The method of claim 25, further comprising irradiating the catalyst with blue color diode light.

27. The method of claim 25, further comprising conducting electric current to the catalyst.

28. A method for generating electricity from a fuel cell, comprising:
providing,
(a) a first electrode,
(b) a second electrode formed from a carbon material selected from
5 the group consisting of fullerene, carbon nanotube, carbon nanohorn, carbon
nanofiber and metal encapsulated fullerene, and
(c) an ion exchange membrane positioned between the first electrode
and the second electrode;
directing oxygen to the first electrode; and
10 directing hydrogen to the second electrode.

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29. The method of claim 28, further comprising irradiating the second electrode with blue color diode light.

30. The method of claim 28, further comprising conducting electric current to the second electrode.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 01/16979

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 H01M8/10 H01M4/86		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 H01M		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, PAJ, CHEM ABS Data, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CHE G. ET AL: "Metal Nanocluster-Filled Carbon Nanotubes: Catalytic Properties and Possible Applications in Electrochemical Energy Storage and Production" LANGMUIR, vol. 15, 1999, page 750-758 XP000964916 page 750, column 2, line 16 -page 751, column 1, line 1 page 754, column 2, line 31 - line 46 figure 1 --- -/--	1-3, 5-12, 14, 16-20, 22-25, 27, 28
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C.		
<input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents: <div style="display: flex; justify-content: space-between;"> <div style="width: 48%;"> <p>*A* document defining the general state of the art which is not considered to be of particular relevance</p> <p>*E* earlier document but published on or after the international filing date</p> <p>*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>*O* document referring to an oral disclosure, use, exhibition or other means</p> <p>*P* document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 48%;"> <p>*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>*Z* document member of the same patent family</p> </div> </div>		
Date of the actual completion of the international search 26 February 2002		Date of mailing of the international search report 05/03/2002
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3018		Authorized officer Riba Vilanova, M

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 01/16979

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CHE G ET AL: "CARBON NANOTUBULE MEMBRANES FOR ELECTROCHEMICAL ENERGY STORAGE AND PRODUCTION" NATURE, MACMILLAN JOURNALS LTD. LONDON, GB, vol. 393, no. 6683, 28 May 1998 (1998-05-28), pages 346-349, XP000960755 ISSN: 0028-0836 page 348, line 7 - line 43 figures 3,4	1-3, 5-12,14, 16-20, 22-25, 27,28
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X	PATENT ABSTRACTS OF JAPAN vol. 1996, no. 06, 28 June 1996 (1996-06-28) & JP 08 031444 A (JAPAN STORAGE BATTERY CO LTD), 2 February 1996 (1996-02-02) abstract	1-3, 5-12,14, 16-20, 22-25, 27,28
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Information on patent family members

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